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THE CRYSTAL AND MOLECULAR STRUCTURE OF THE 1:1 COMPLEX FORMED BETWEEN 4-PHENYLPYRIDINE-1-OXIDE AND COPPER(II) CHLORIDE

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The crystal structure of the binuclear complex formed between 4-phenylpyridine-1-oxide and copper(II) chloride has been determined. Single crystal X-ray counter methods were used to collect 3648 non-zero reflections. The complex crystallizes in the triclinic space group $P\bar{1}$ with a unit cell of dimensions $a = 10.069(8)$ Å, $b = 12.857(5)$ Å, $c = 10.143(5)$ Å, $\alpha = 106^\circ 10(5)'$, $\beta = 99^\circ 45(5)'$, and $\gamma = 97^\circ 2(5)'$. The observed and calculated densities are 1.709 and 1.704 g. cm⁻³, respectively. The structure was refined by least-squares methods to a conventional R factor of 0.058. The complex consists of two independent oxygen-bridged dimers of empirical formulas $[(C_{11}H_9NO)CuCl_2]_2$ and $[(C_{11}H_9NO)CuCl_2 \cdot H_2O]_2$. The Cu(II) ions in one dimer are four-coordinate and contain two bridging Cu—O bonds of 1.978(5) and 1.986(4) Å. The Cu(II) ions in the second dimer are five coordinate with a water molecule occupying the apical site of a square-based pyramidal geometry. The Cu—O (w) bond is 2.356(7) Å and the two bridging Cu—O bonds are 1.980(5) and 2.040(6) Å. The magnetic properties of the solid are rationalized in terms of an average contribution from the two dimers.

INTRODUCTION

The 1:1 aromatic N-oxide complexes of copper(II) halides exhibit reduced magnetic moments at room temperature. The structures of di- μ -(Pyridine-1-oxide)-bis(dichlorocopper(II))¹⁻³ and di- μ -(pyridine-1)-bis(dibromocopper(II))⁴ have been determined. The complexes are oxygen-bridged dimers and the exchange interaction occurs through the bridging ligands. The ligands expand the $d_{x^2-y^2}$ magnetic orbitals of the copper(II) ion and a positive overlap results in an antiferromagnetic exchange interaction. The electronic configuration of the bridging oxygen atoms should affect the $d_{x^2-y^2}$ orbitals of the copper(II) ion, and therefore influence the magnitude of the exchange interaction. Substituents on the pyridine ring effect to some extent the electron distribution around the oxygen atom, and if the geometry of all 1:1 complexes were identical, the substituent might indirectly affect the magnitude of the exchange interaction. A correlation between the exchange energy and Taft's σ_R values was reported for several complexes;⁵ however, later investigators reported no correlation existed when a more extended series of complexes was considered.^{6,7} A series of 4-substituted pyridine-1-oxide copper (II) chloride complexes required two lines to cor-

relate the exchange energy and the Taft σ_R parameters.⁸ It was suggested that a lack of correlation might be due to differences in structure which would mask any substituent effect. The 4-phenylpyridine-1-oxide complex with copper(II) chloride does not follow the same correlation line as the pyridine-1-oxide complex whose structure has been reported. We would like to report the structure of the 1:1 complex formed between 4-phenylpyridine-1-oxide and copper(II) chloride.

EXPERIMENTAL

The complex is prepared by mixing ethanol solutions of 4-phenylpyridine-1-oxide and copper(II) chloride in a 1:1 molar ratio. The complex was recrystallized from ethanol at room temperature by slow evaporation. Carbon, hydrogen and nitrogen analyses were made by Scandinavian Microanalytical Laboratory. Copper was determined by an EDTA titration.⁹ Found: Cu, 20.25; C, 41.67; H, 3.31; N, 4.39. Calcd. for $C_{11}H_9NOCuCl_2$; Cu, 20.79; C, 43.22; H, 2.97; N, 4.58. Calcd. for $C_{11}H_9NOCuCl_2 \cdot 1/2 H_2O$: Cu, 20.19; C, 41.99; H, 3.18; N, 4.45. The existence of water in the complex was established by the structural analysis.

Many of the crystals were twinned, but a green

irregular shaped crystal was found to be suitable for intensity measurements. The crystal was approximately $.240 \times .190 \times .593$ mm., and it was mounted with the long axis coincident with the spindle axis of the Weissenberg camera. Preliminary photographs indicated the crystal to be triclinic and the axis coincident with the spindle axis was designated as a . Unit cell parameters were measured from a axis rotation and OkI Weissenberg photographs using superimposed NaCl powder lines as an internal standard, ($a = 5.649$ Å). All film data were taken at room temperature using zirconium-filtered molybdenum radiation ($\lambda = 0.71069$ Å).

Crystal Data

(There are two independent dimeric molecules in the unit cell.)

Dimer I

$[(C_6H_5-C_5H_4NO)CuCl_2]_2$ Mol. Wt. = 611

Dimer II

$[(C_6H_5-C_5H_4NO)CuCl_2 \cdot H_2O]_2$ Mol. Wt. = 647
 $a = 10.069(8)$ Å, $b = 12.857(5)$ Å, $c = 10.143(5)$ Å
 $\alpha = 106^\circ 10(5)$, $\beta = 99^\circ 45(5)$, $\gamma = 97^\circ 2(5)$

No systematic absences were observed

Space group: $P\bar{1}$

$Z = 2$ (one dimer molecule of each type), $V = 1222.4$ Å³, $T = 22.661$ cm⁻¹ $D_{obs} = 1.709$ g. cm⁻³, $D_{calc.} = 1.704$ g. cm⁻³

The errors in the cell edges are the average deviations calculated from the measurement of several high angle reflections or layer lines. The error in the angle is the average deviation calculated from several measurements of the same angle. The density was measured by the flotation technique using a mixture of chloroform and bromoform. The unit cell contains one anhydrous dimeric molecule and one hydrated dimeric molecule.

Three-dimensional intensity data through the eleventh level (OkI to $llkl$) were collected with a Philips PAILRED diffractometer using equi-inclination geometry and the continuous ω -scan technique. $MoK\alpha$ radiation and a graphite monochromator crystal ($d_{002} = 3.354$ Å) were used. The ω -scan range was varied from 2.2° for the

zero level to 3.6° for the eleventh level and a speed of $1^\circ/\text{min.}$ was used throughout. Background counts of 40 seconds were taken, and reflections of the type hkl , $hk\bar{l}$, $h\bar{k}l$, and $h\bar{k}\bar{l}$ were scanned up to a 2θ limit of 55° . The zero level reflections OkI , $O\bar{k}\bar{l}$ and $O\bar{k}l$, $Ok\bar{l}$ were equivalent within experimental error. All equivalent reflections were averaged to give a unique set of data. A total of 5085 non-equivalent reflections were measured and 3648 were found to satisfy the condition $I_o \geq 2\sigma(I_o)$ and were considered observed. The calculation of standard deviations of the intensities and structure factors are described elsewhere.⁴ The intensities of several reference reflections were monitored during the data collection period, and differences were observed to be less than 2%. The levels were scaled together, and the scaling was checked during the refinement procedure.

The data were corrected for absorption.¹⁰ The crystal faces were measured accurately, and the crystal volume was calculated to be 0.0139 mm³. The maximum and minimum transmission factors were calculated to be 0.772 and 0.666.

The scattering factors of Cromer and Waber¹¹ were used for all non-hydrogen atoms. The scattering factors of the copper(II) ions and the chloride ions were corrected for the real part of the anomalous dispersion using the values of Cromer.¹² The hydrogen scattering factors were those calculated by Stewart, Davidson and Simpson.¹³

Structure Determination

A three-dimensional Patterson map was calculated with the origin peak removed. Vectors associated with the copper(II) ions were identified, and the structure was solved by conventional techniques. Block-diagonal least-squares refinement was followed by five cycles of full-matrix least-squares refinement using 1529 of the strongest reflections. The temperature factors of the copper, chlorine and oxygen atoms were treated anisotropically. The conventional R factor was .0371 and $R(\text{wtd})$ was .0395. Description of the weighting scheme and refinement has been given elsewhere.⁴ All shifts in the parameters were less than one-tenth of the estimated standard deviations of the parameter. The standard deviations were calculated from the inverse of the normal-equations matrix of the last cycle of refinement. The final positional and thermal parameters are given in Table I.

Ring hydrogen positions were calculated and

TABLE I

Atomic and thermal parameters for the 1 : 1 complex formed between copper(II) chloride and 4-phenylpyridine-1-oxide

ATOM	X ^a	Y	Z	B or B ₁₁ ^b	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Cu(1)	.0850 (1)	-.1003 (1)	-.0212 (1)	2.15 (6)	2.15 (6)	3.82 (7)	.38 (9)	1.95 (11)	2.72 (9)
Cu(2)	.4131 (1)	.0651 (1)	.4068 (1)	1.82 (5)	2.39 (6)	2.82 (6)	-.96 (9)	-.11 (7)	2.32 (9)
Cl(1)	.0197 (3)	-.2721 (2)	-.0348 (4)	4.30 (15)	2.27 (13)	7.70 (22)	1.05 (20)	5.10 (30)	3.62 (27)
Cl(2)	.2826 (3)	-.1159 (2)	-.0861 (3)	2.89 (11)	3.20 (13)	3.83 (14)	1.00 (19)	3.08 (19)	1.72 (23)
Cl(3)	.1887 (3)	.0335 (3)	.3094 (4)	2.13 (10)	4.45 (15)	6.50 (19)	-.91 (19)	-1.12 (22)	4.82 (27)
Cl(4)	.4689 (3)	.2330 (2)	.3989 (3)	3.33 (12)	2.27 (12)	4.87 (16)	-.67 (19)	-1.20 (22)	3.01 (23)
O(1)	-.0813 (6)	-.0506 (6)	.0347 (7)	1.83 (27)	2.52 (31)	4.23 (37)	-.05 (48)	1.69 (53)	3.16 (56)
O(2)	.4048 (6)	-.0697 (6)	.4655 (7)	1.40 (25)	3.06 (32)	3.57 (35)	-1.72 (43)	-.38 (49)	3.52 (56)
O(w)	.4937 (8)	-.0218 (7)	.2064 (8)	4.62 (40)	4.68 (42)	3.13 (39)	2.05 (67)	2.92 (64)	.14 (65)
N(1)	-.1860 (8)	-.1193 (6)	.0549 (8)	2.25 (15)					
C(2)	-.1724 (10)	-.1351 (8)	.1811 (10)	2.60 (18)					
C(3)	-.2740 (10)	-.2074 (8)	.2018 (10)	2.49 (18)					
C(4)	-.3885(9)	-.2617 (8)	.0948 (10)	2.03 (16)					
C(5)	-.3972 (6)	-.2400 (8)	-.0333 (10)	2.27 (18)					
C(6)	-.2941 (10)	-.1675 (8)	-.0530 (11)	2.49 (19)					
C(7)	-.4959 (9)	-.3420 (7)	.1152 (10)	2.20 (17)					
C(8)	-.4661 (11)	-.3934 (10)	.2171 (12)	3.62 (22)					
C(9)	-.5658 (12)	-.4732 (10)	.2332 (12)	3.80 (23)					
C(10)	-.6949 (11)	-.5002 (9)	.1443 (12)	3.37 (21)					
C(11)	-.7279 (12)	-.4488 (9)	.0421 (12)	3.53 (22)					
C(12)	-.6275 (10)	-.3687 (9)	.0273 (11)	2.87 (19)					
N(2)	.2885 (8)	-.1395 (6)	.4521 (8)	2.11 (14)					
C(22)	.2417 (11)	-.2217 (9)	.3327 (11)	3.16 (21)					
C(23)	.1246 (11)	-.2978 (9)	.3162 (11)	3.24 (21)					
C(24)	.0571 (9)	-.2871 (8)	.4279 (10)	2.01 (16)					
C(25)	.1075 (11)	-.1980 (9)	.5480 (11)	3.19 (21)					
C(26)	.2243 (11)	-.1243 (9)	.5580 (11)	3.11 (21)					
C(27)	-.0588 (9)	-.3732 (8)	.4239 (10)	2.20 (17)					
C(28)	-.0710 (11)	-.4803 (9)	.3332 (11)	3.16 (20)					
C(29)	-.1739 (12)	-.5646 (10)	.3354 (12)	3.82 (23)					
C(30)	-.2614 (12)	-.5397 (10)	.4244 (12)	3.90 (23)					
C(31)	-.2523 (12)	-.4335 (10)	.5125 (13)	3.91 (23)					
C(32)	-.1498 (10)	-.3486 (9)	.5100 (11)	2.94 (20)					
H(2) ^c	-.084	-.092	.264	2.0					
H(3)	-.265	-.222	.302	2.0					
H(5)	-.485	-.280	-.118	2.0					
H(6)	-.300	-.150	-.152	2.0					
H(8)	-.365	-.372	.285	2.0					
H(9)	-.543	-.513	.313	2.0					
H(10)	-.771	-.563	.155	2.0					
H(11)	-.829	-.470	-.025	2.0					
H(12)	-.651	-.328	-.051	2.0					
H(22)	.295	-.229	.248	2.0					
H(23)	.086	-.364	.219	2.0					
H(25)	.055	-.186	.634	2.0					
H(26)	.263	-.055	.652	2.0					
H(28)	-.002	-.498	.262	2.0					
H(29)	-.184	-.648	.267	2.0					
H(30)	-.340	-.604	.426	2.0					
H(31)	-.323	-.416	.582	2.0					
H(3)	-.143	-.265	.575	2.0					

^aNumbers in parentheses are estimated standard deviations of the last significant digit.^bAnisotropic thermal parameters have the form $\exp [-.25 (B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^{*}b^{*} + 2B_{13}hla^{*}c^{*} + 2B_{23}kib^{*}c^{*})]$.^cHydrogen atom parameters were used to calculate structure factors but they were not refined.

TABLE II

Interatomic distances and bond angles for the 1 : 1 complex formed between copper(II) chloride and 4-phenylpyridine-1-oxide^a

Molecule 1					
Cu(1)—Cl(1)	2.184 (2)	N(1)—C(6)	1.348 (12)	C(7)—C(8)	1.386 (12)
Cu(1)—Cl(2)	2.212 (2)	C(2)—C(3)	1.379 (10)	C(8)—C(9)	1.407 (12)
Cu(1)—O(1)	1.978 (5)	C(3)—C(4)	1.395 (12)	C(9)—C(10)	1.393 (14)
Cu(1)—O(1')	1.986 (4)	C(4)—C(5)	1.394 (12)	C(10)—C(11)	1.393 (13)
O(1)—N(1)	1.371 (7)	C(5)—C(6)	1.386 (10)	C(11)—C(12)	1.409 (11)
N(1)—C(2)	1.337 (12)	C(4)—C(7)	1.481 (9)	C(12)—C(7)	1.409 (12)
Molecule 2					
Cu(2)—Cl(3)	2.189 (2)	N(2)—C(26)	1.327 (12)	C(27)—C(28)	1.404 (11)
Cu(2)—Cl(4)	2.244 (2)	C(22)—C(23)	1.390 (11)	C(28)—C(29)	1.411 (12)
Cu(2)—O(2)	1.980 (5)	C(23)—C(24)	1.400 (13)	C(29)—C(30)	1.367 (15)
Cu(2)—O(2')	2.040 (6)	C(24)—C(25)	1.386 (13)	C(30)—C(31)	1.390 (14)
Cu(2)—O(w)	2.356 (7)	C(25)—C(26)	1.386 (11)	C(31)—C(32)	1.415 (12)
O(2)—N(2)	1.347 (7)	C(24)—C(27)	1.492 (9)	C(32)—C(27)	1.375 (12)
N(2)—C(22)	1.332 (12)				
Nonbonding distances					
Cu(1)—Cl(3)	3.231 (4)	Cl(4)—H(6')	2.63	O(2)—O(2')	2.319 (7)
Cu(1)—Cu(1)	3.236 (1)	O(w)—Cl(2)	3.162 (7)	Cl(21')—H(12')	2.98
O(1)—O(1')	2.289 (7)	O(w)—Cl(21)	3.293 (7)	Cl(21')—(26')	2.96
Cl(3)—H(2)	2.91	O(w)—H(26')	2.54	Cl(1)—H(90)	2.91
Cl(3)—H(6')	2.75	Cu(2)—Cu(2')	3.285 (1)		
Cl(1)Cu(1)Cl(2)	98.2 (1)	N(1)C(2)C(3)		118.1 (8)	
Cl(1)Cu(1)O(1)	95.2 (1)	C(2)C(3)C(4)		121.0 (8)	
Cl(1)Cu(1)O(1')	161.7 (5)	C(3)C(4)C(5)		117.8 (7)	
Cl(1)Cu(1)Cl(3)	106.4 (1)	C(3)C(4)C(7)		121.3 (8)	
Cl(2)Cu(1)O(1')	96.0 (2)	C(4)C(5)C(6)		120.5 (8)	
Cl(2)Cu(1)O(1)	166.4 (6)	C(5)C(6)N(1)		118.1 (8)	
Cl(2)Cu(1)Cl(3)	101.1 (1)	C(4)C(7)C(8)		120.3 (7)	
O(1)Cu(1)Cl(3)	76.4 (2)	C(12)C(7)C(8)		119.9 (7)	
O(1)Cu(1)O(1')	70.5 (2)	C(7)C(8)C(9)		120.7 (9)	
O(1')Cu(1)Cl(3)	82.0 (2)	C(8)C(9)C(10)		118.9 (9)	
Cu(1)O(1)Cu(1')	109.4 (2)	C(9)C(10)C(11)		121.5 (8)	
Cu(1)O(1)N(1)	123.0 (4)	C(10)C(11)C(12)		119.1 (9)	
O(1)N(1)C(6)	118.5 (7)	C(11)C(12)C(7)		119.9 (9)	
C(6)N(1)C(2)	124.4 (7)				
Molecule 2					
Cl(3)Cu(2)Cl(4)	99.3 (1)	N(2)C(22)C(23)		120.8 (9)	
Cl(3)Cu(2)O(2)	94.8 (2)	C(22)C(23)C(24)		118.8 (9)	
Cl(3)Cu(2)O(2')	162.5 (5)	C(23)C(24)C(25)		118.0 (7)	
Cl(3)Cu(2)O(w)	98.9 (2)	C(23)C(24)C(27)		121.5 (7)	
Cl(4)Cu(2)O(2')	94.0 (1)	C(24)C(25)C(26)		120.5 (9)	
Cl(4)Cu(2)O(2)	163.1 (7)	C(25)C(26)N(2)		119.7 (9)	
Cl(4)Cu(2)O(w)	95.9 (2)	C(24)C(27)C(28)		118.8 (7)	
O(2)Cu(2)O(w)	91.1 (2)	C(32)C(27)C(28)		120.7 (7)	
O(2)Cu(2)O(2')	70.4 (2)	C(27)C(28)C(29)		119.5 (8)	
O(2')Cu(2)O(w)	90.9 (3)	C(28)C(29)C(30)		119.3 (8)	
Cu(2)O(2)Cu(2')	109.6 (2)	C(29)C(30)C(31)		121.8 (8)	
Cu(2)O(2)N(2)	124.5 (4)	C(30)C(31)C(32)		119.2 (9)	
O(2)N(2)C(22)	118.9 (7)	C(31)C(32)C(27)		119.5 (8)	
C(26)N(2)C(22)	122.1 (7)				

^aNumbers in parentheses are estimated standard deviations of the last significant digit.

their inclusion in a structure factor calculation yielded $R = .0340$ and $R(\text{wtd}) = .0380$ for the 1529 strongest reflections. The addition of the hydrogen atoms to the model was significant at the 0.005 confidence level.¹⁴ Calculation of structure factors for all 3648 observed reflections gave $R = .0583$ and $R(\text{wtd}) = .0552$. A least-squares refinement using all 3648 observed reflections was not attempted because of limited core memory and limited computer funds. A ratio of at least five reflections per parameter to be refined usually is considered to be adequate. A table of the final observed and calculated structure factors may be obtained from the editor.

A final three-dimensional difference Fourier was calculated and showed several peaks about the ring atom positions of magnitude $0.4 \text{ e}/\text{\AA}^3$. These peaks were indicative of anisotropic thermal motion associated with these atoms. Because of the number of parameters, no attempt was made to anisotropically refine the ligand thermal parameters. The hydrogen atoms of the water molecule were not discernable in the final difference map.

DISCUSSION

The two independent dimeric molecules in the unit cell are oxygen-bridged and contain a center of inversion. Projections of the contents of the unit cell on the *ac* and *ab* planes are shown in Figures 1 and 2. The calculated bond lengths and angles, along with the estimated standard deviations, are given in Table II. The numbering system is consistent with that used in the Figures.

The coordination geometries around the copper ions in the two complexes are not identical. Figure 3 shows the geometry around two of the ions. The copper ions in one complex are four coordinate and exhibit a *cis*-square planar geometry with Cl(3) from an adjacent complex occupying an axial site at a distance of 3.231 Å. This distance is much longer than the Cu-Cl distance of 2.836 Å observed in the pyridine-1-oxide complex,³ and the interaction would have little effect on the chemical or physical properties of the Cu(1) ion. The O(1)Cu(1)O(1') angle is 70.5° and is consistent with the angles of 72,¹⁻³ 70⁴ and 71¹⁵ degrees found in other oxygen-bridged complexes. The other angles about the Cu(1) ion are consistent with ligand-ligand repulsion. The two Cu(1) atoms and the bridging oxygen atoms define a plane, and Cl(2) lies .05 Å above the plane while Cl(1) lies .44 Å below the plane. Cl(2) lies

within 2.98 Å and 2.96 Å of pyridine hydrogens from adjacent complexes and probably is hydrogen bonded to the water molecule. Cl(1) lies within 2.91 Å of a phenyl hydrogen from an adjacent complex. If the chlorine atoms lay within the copper-oxygen plane, some of the interaction distances would be shorter.

The copper ions in the second complex are five coordinate and the geometry about Cu(2) can be described as a square-based pyramid. The apical site is occupied by the water molecule at 2.356 Å. The two water molecules lie *trans* with respect to the copper-oxygen plane. The angles within the square base are similar to those found in the other complex. The Cu—O bond lengths are longer than those found in the four coordinate complex, and the 2.040 Å Cu—O bond length is at least nine standard deviations longer than those in the four coordinate complex. The lengthening of the bond is attributed to the presence of the water molecule at the apical site. This elongation has been observed for other complexes in the series and can be rationalized in terms of reduced positive charge on the Cu(II) ion. The OCu(2)O(w) angles are 91.1° and 90.9° while the ClCu(2)O(w) angles are 98.9° and 95.9° Cl(3) lies .38 Å out of the plane defined by the Cu and oxygen atoms while Cl(4) lies .26 Å from the plane. Both atoms are found on the opposite side of the plane from the water molecule.

Although the hydrogen atoms of the water molecule were not located in the difference Fourier map, the presence of hydrogen bonding in this complex is highly probable. The Cl(2)—O(w) and Cl(21)—O(w) distances of 3.162 Å and 3.293 Å indicate the atoms are close enough for hydrogen bonding.¹⁶⁻¹⁹ Each water molecule is within hydrogen bond distance of a Cl(2) from two different molecules, and conversely, each Cl(2) is within hydrogen bond distance of water molecules from two different molecules. The Cl(2)O(w)Cl(21) angle of 94.2° is consistent with the simultaneous formation of two hydrogen bonds, but the Cu—O(w) bond makes an angle of 47° with the plane of these three atoms. This would imply one specific hydrogen bond is formed or else there is a statistical distribution between the two positions.

Least-squares planes fitted to the pyridine and phenyl rings of the ligand associated with the four-coordinate dimer indicate the rings are planar within .004 Å. The C—C bonds average 1.388 Å in the pyridine ring and 1.398 Å in the phenyl ring. The N—C bond lengths of 1.348 Å and 1.337 Å and the N—O bond length of 1.371 Å are normal.

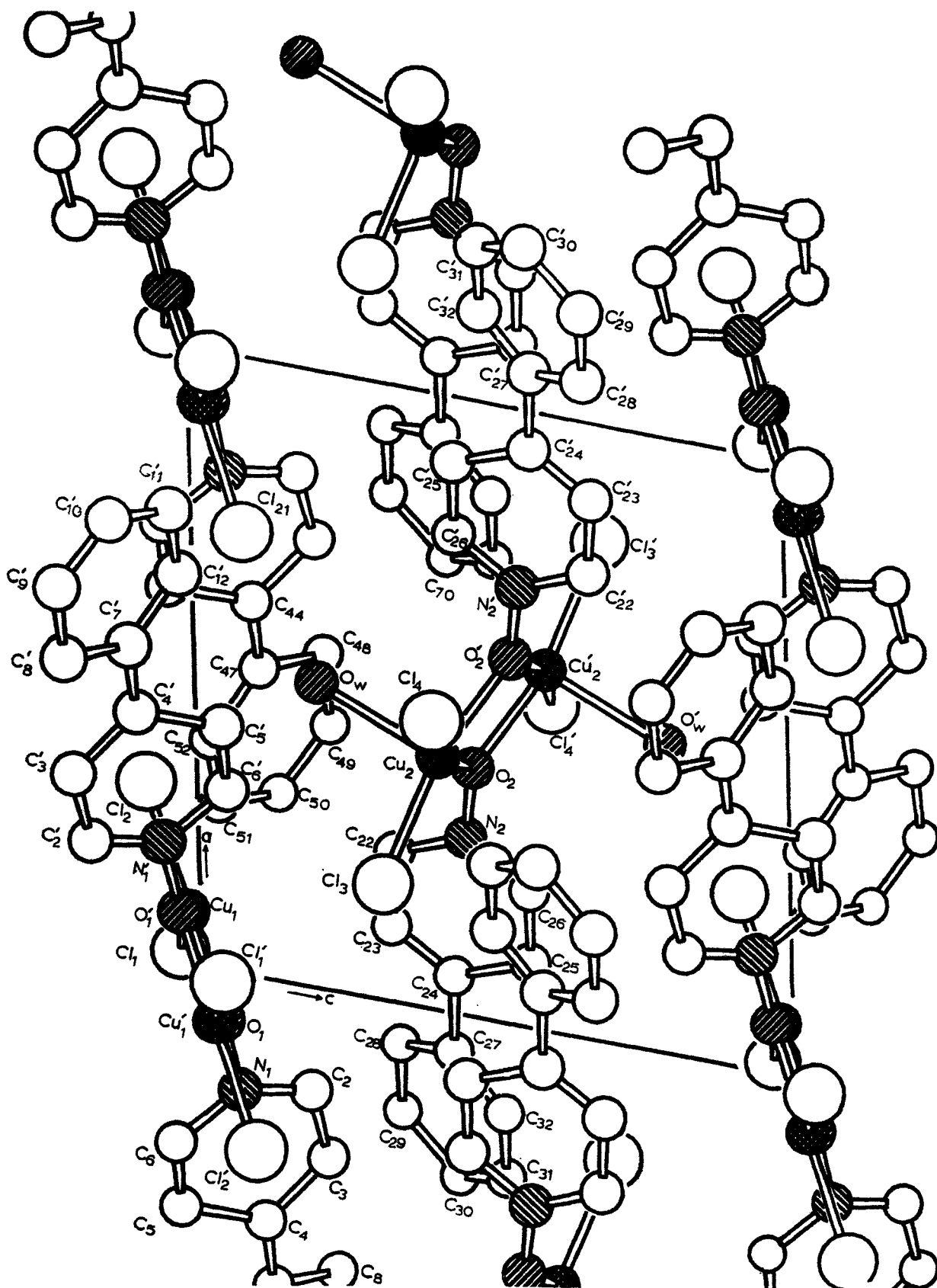
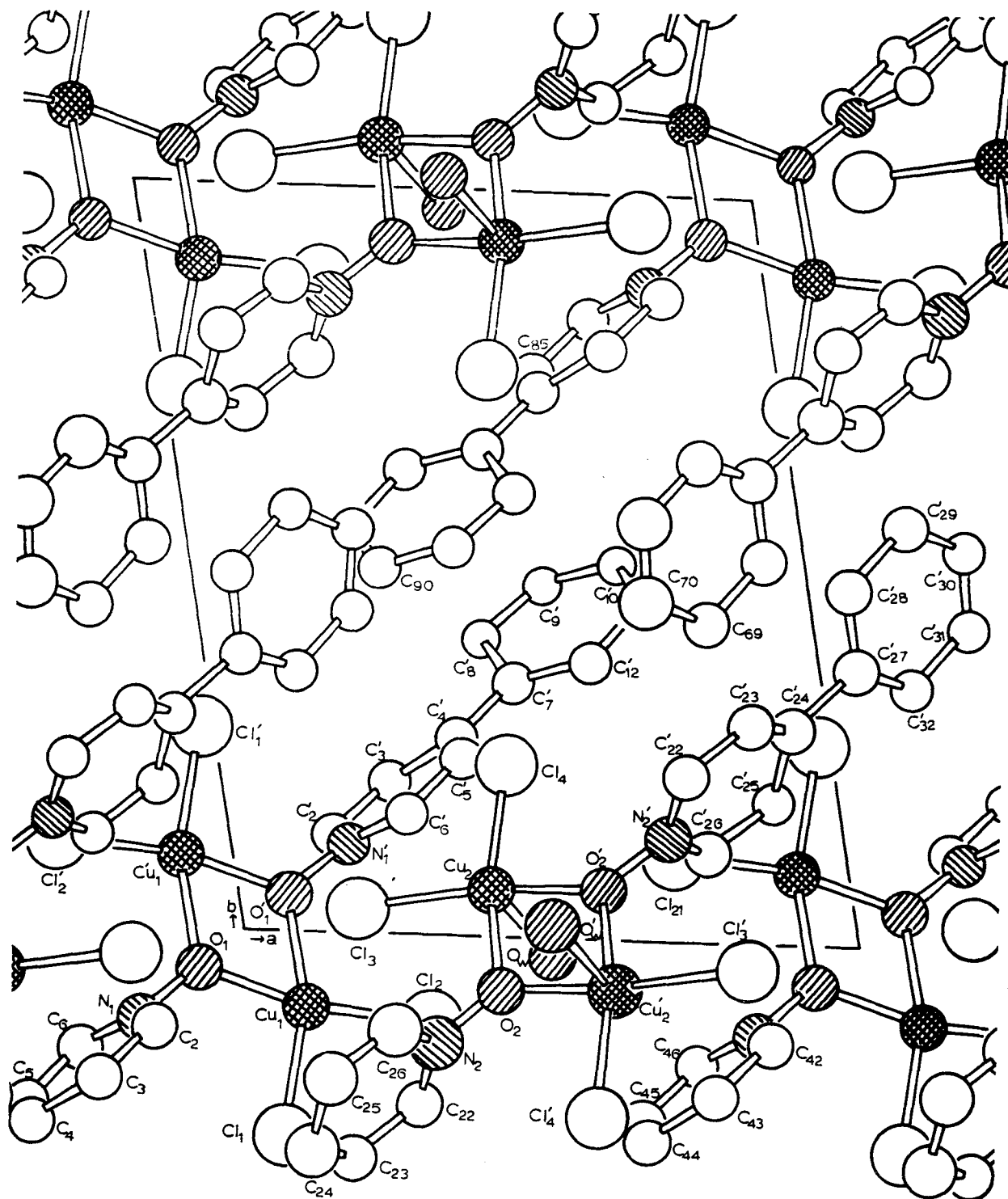


FIGURE 1 Contents of unit cell projected onto the ac plane.
 (Tables are in the files of the Editor and copies are available for review)

FIGURE 2 Contents of unit cell projected onto the ab plane.

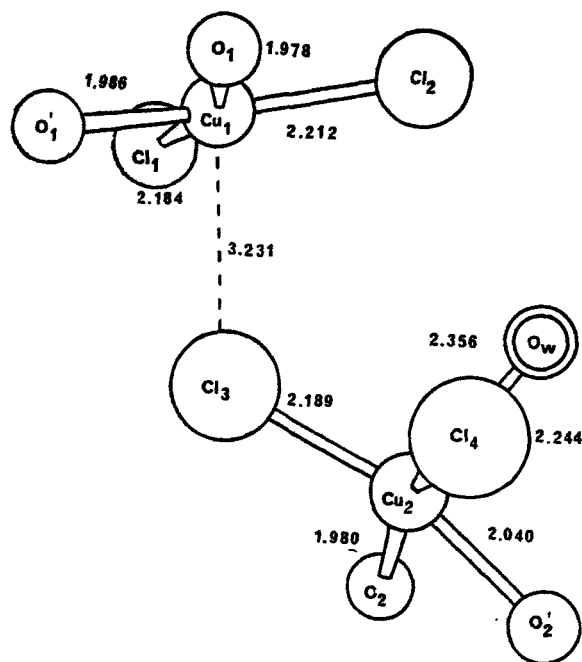


FIGURE 3 Illustration of the coordination of one of the copper ions in each complex. The oxygen atoms are bridged to other copper ions, but they have been excluded for clarity.

The normals to the two rings make an angle of 22.4° . The angle defined by the lines $N(1)-C(4)$ and $C(7)-C(10)$ is 175° . The $C-C$ bond length between the two rings is 1.48 \AA . A survey of similar systems indicates the $C-C$ bond lengths between two rings are approximately 1.50 \AA whether the rings are coplanar or twisted.²⁰⁻²² The orientation of the rings is determined by crystal packing. The pyridine ring plane makes an angle of 85.1° with the copper-oxygen plane and the $N-O$ bond makes an angle of 10° with this plane.

Least-squares planes fitted to the pyridine and phenyl rings of the ligand associated with the five coordinate dimer indicate the rings are planar within $.011 \text{ \AA}$ and $.008 \text{ \AA}$, respectively. The average $C-C$ bond lengths in the two rings are 1.392 \AA and 1.393 \AA . The $N-C$ bond lengths of 1.327 \AA and 1.332 \AA and the $N-O$ bond length of 1.347 \AA are normal. The angle between the normals to the two rings is 29.6° and the $C-C$ distance between the two rings is 1.49 \AA . The angle defined by the lines $N(2)-C(24)$ and $C(27)-C(30)$ is 169° . The pyridine ring makes an angle of 79.7° with the copper-oxygen plane, and the $N-O$ bond makes an angle of 8.6° with this plane.

The temperature dependence of the magnetic sus-

ceptibility can be rationalized. The high temperature susceptibility was not reproducible and is associated with the loss of water. The room temperature magnetic moment of $.32 \text{ B.M.}$ is lower than the moment associated with the pyridine-1-oxide complex. The pyridine-1-oxide complex is five-coordinate due to an intermolecular interaction with a chlorine atom of an adjacent complex. Since the five coordinate dimer and the pyridine-1-oxide complex have similar geometries and bond lengths around the copper(II) ions, the magnetic moments should be similar. The four coordinate complex would exhibit a lower magnetic moment due to the shorter $Cu-O$ bonds and square-planar geometry. The observed magnetic moment and the exchange energy are averages for the two types of complexes. Any substituent effect would be negligible compared to the perturbation created by changes in geometry and coordination. While other members in this series probably do not contain coordinated water, structural changes may account for the lack of correlation with any substituent parameter.

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